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High temperature thermoelectric power measurements of $YBa_2Cu_3O_{7-\delta}$ and conclusions concerning the electronic structure close to E_F

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In honor of Martin Peter's 60th birthday.

Abstract. Thermoelectric power (TEP) measurements were carried out on $YBa_2Cu_3O_{7-\delta}$ up to 950°C, in air and in flowing oxygen at 1 bar. Below 700 K the TEP is small, and increases rapidly above it reaching, at 1200 K, +140 μV/K in air and +120 μV/K in oxygen. The results are interpreted in terms of a model of a narrow band, which is full for $\delta = 1$ and half filled for $\delta = 0$. Possible origins for such a narrow band are discussed.

A recent publication of our laboratory [1] reported a steep increase with temperature of the resistivity (ρ) of $YBa_2Cu_3O_{7-\delta}$ (YBaCuO) samples on heating above room temperature. It was proposed there that this increase was mainly due to variations in the transport mechanism and not in the carrier concentration. In order to test this, we investigate here the dependence of the carrier concentration on the temperature and the oxygen content of YBaCuO at high temperatures, by measuring the thermoelectric power (TEP).

The measurements were carried out on a ceramic rod of YBaCuO up to 950°C in oxygen at 1 bar pressure and in air. The measurements were taken over a long period of time in order to achieve thermal equilibrium. In Fig. 1 we present the temperature (T) dependence of the absolute TEP (S) of a sample of YbaCuO in air (a) and in oxygen at 1 bar (b). Inspection of the TEP results, at fixed oxygen pressure, shows that while S remains very low between room temperature and 700 K, it increases steeply with temperature above 700 K up to about +120 μV/K in oxygen and to +140 μV/K in air at 1200 K. In Ref. 1 it was shown that 700 K is also the temperature where the slope of the plot of log (ρ) *vs* T changes considerably.

From thermogravimetric measurements [2] it was shown that at constant oxygen pressure $P(O_2)$, the oxygen deficiency parameter δ (appearing in the

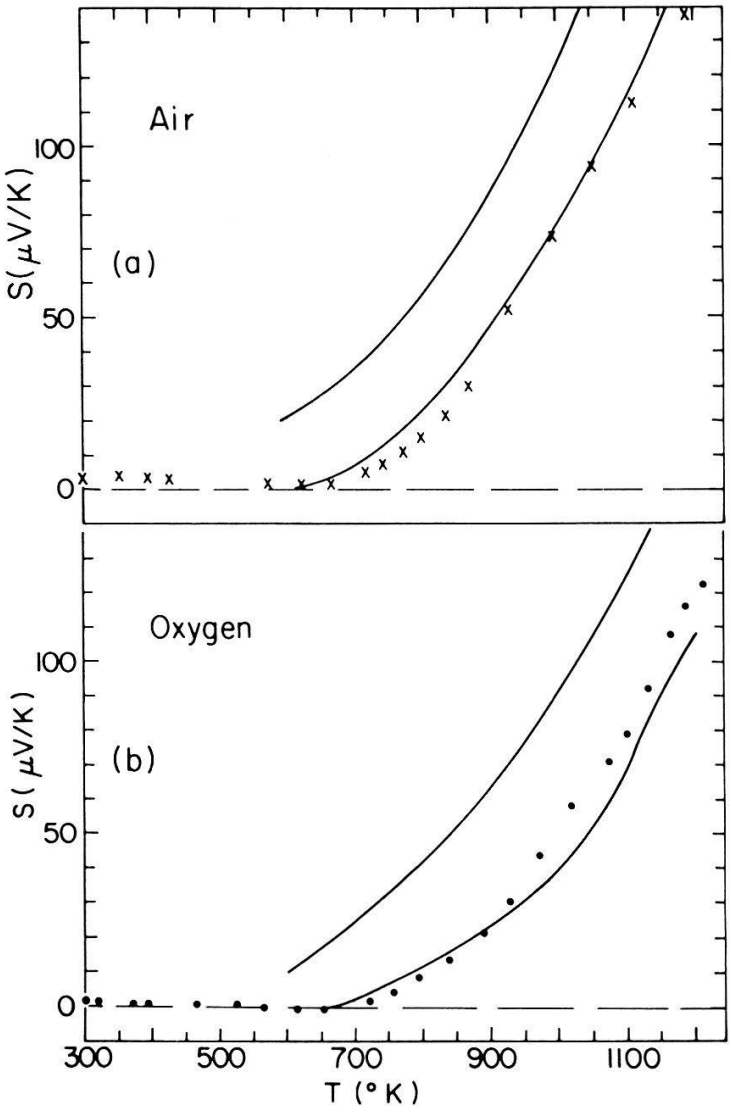

Figure 1
The temperature dependence of the TEP in YBaCuO in air (a) and in oxygen at 1 bar (b). The measured values are shown by points and crosses; the range of values calculated by equation (1), using $\delta(T)$ taken from the different reports in Ref. 2, is shown by continuous lines.

formula $YBa_2Cu_3O_{7-\delta}$) starts increasing quite rapidly with temperature above 700 K. We conclude that S increases when δ increases, the increase in δ being due either to increase in temperature, or to reduction of oxygen pressure. We therefore assume that a simple relation exists between S and δ at high temperatures.

At these temperatures, our measured values of S in Fig. 1(a, b) are too large for a simple metal and atypically low for a semiconductor. They are in the range characteristic of a conductor with a partially filled narrow [3] conduction band. A model, consistent with the TEP data, is based on the assumptions that at high temperatures: (a) $Yba_2Cu_3O_6$ has a full narrow [3] top band. (b) The oxygen atoms added to the system enter with charge $-v$ each, creating v holes in the narrow band; our data are consistent with v either 1 or 2. (c) The number of electron states per unit cell (=formula unit) in the narrow band is $2v$, and the

carriers in it are uncorrelated (namely, within this band the Coulomb integral U is small [3]). Note, however, that this small U represents Coulomb interactions within a unit cell and not within an atom, and our model does not contradict the existence of strong intraatomic correlations.

By assumption (b), n – the number of electrons (per unit cell) in the top band, is given by: $n = v(1+\delta)$. For a narrow band, containing two uncorrelated states ($v = 1$), the assumptions (a) and (c), yield the following expression [4] for the TEP:

$$S = (k/e) \ln [n/(2-n)] = (k/e) \ln [(1+\delta)/(1-\delta)]. \quad (1)$$

The same expression for $S(\delta)$ is obtained also for $v = 2$ by considering two degenerate bands as described before.

In order to compare the experimentally measured S with that calculated from Equation (1), we used the available data on $\delta(P(O_2), T)$ [2]. The spread of the published data is quite broad, and there is therefore a degree of uncertainty in the comparison between the calculated and the measured TEP. In Fig. 1(a, b) we also show the range of values of $S(T)$ calculated by Equation (1), where the dependence $\delta(P(O_2), T)$ is taken from Ref. 2. The individual plots from the different reports in Ref. 2 lie between the top and bottom limiting lines in Fig. 1(a, b) (often intersecting each other). In spite of the wide spread in the calculated values, based on the different published reports, one can see that the temperature dependence of the experimental and the calculated values $S(T)$ are very similar. The lower edge of the calculated range (corresponding to the lower value of $\delta(T)$) is closer to the experimental points.

Note that below 700 K, the TEP is low, and it is impossible to distinguish between the results of the narrow-band model proposed here, and of a wide band model (which automatically yields low TEP). Also note that, although the present model is rather crude, it is clear that our TEP results could not be accounted for by an alternative correlated electrons narrow-band model [4] (where, due to a large [3] U, there is only one electron state per unit cell).

Important features of the narrow band postulated here are that its width and its effective Coulomb integral U are each less than 1000 K. In principle, there might be several sources for this narrow band. First-principles band-structure calculations [5], for $\delta = 0$ and $\delta = 1$ (supported for $\delta \simeq 0$ by positron annihilation measurements [6]) predict that the Fermi level (E_F) lies within a wide band, and that it is close to (for $\delta = 1$) or within (for $\delta = 0$) a narrow band which corresponds to the antibonding $dp\pi$ levels of the O4-Cul-O4 clusters [7]. The existence of a wide band, in addition to the narrow band at E_F, would obviously modify the results of our simple model above 700 K. However, this would change when the effect of intraatomic electron correlations is introduced (it should be stressed that our postulated small U mentioned above represents correlations within a unit cell which includes 12–13 atoms). Models based on strong electron correlations [8], predict that they will induce a Hubbard gap and/or considerable narrowing of a partly filled wide band.

Since intraatomic Coulomb integrals in YBaCuO are expected to be not less

than 1 eV, the assumed small U of our model has to represent an interatomic Colomb integral (probably not even between nearest neighbors) within the unit cell. This can occur (in a tight-binding representation) if the narrow band consists, to a good approximation, only of orbitals of atoms that have $2v$ equivalent sites per unit cell (see assumption (c)). Electron correlations would then prevent double occupancy of an atom, but not of a unit cell. The effect of randomness in the distribution of the added O1 atoms (for $\delta < 1$) on the narrow band is expected to be as small as the interatomic U parameter. In addition to band narrowing, many-body effects could also suppress the hybridization between orbitals of different atoms (copper and oxygen) with different intraatomic Coulomb integrals.

We propose three possible orbital origins for our narrow band. Within the first possibility, the added O1 atoms enter as O^{-2} ions ($v = 2$), and the narrow band consists of p orbitals of the almost equivalent O2–O3 sites (four per unit cell). The Cu2 atoms should then be very close to Cu^{+2} ionization states, and the O2–O3 atoms fluctuate between O^{-2} and O^{-1} states, becoming O^{-2} for $\delta = 1$. The second possibility assumes that the added O1 atoms enter as O^{-1} ($v = 1$), and the narrow band consists of the d orbitals of the Cu2 atoms (two equivalent atoms per unit cell). The O2–O3 atoms should then be very close to an O^{-2} ionisation state, and the Cu2 atoms fluctuate between Cu^{+2} and Cu^{+3} states, becoming Cu^{+2} for $\delta = 1$. Finally, the third possibility assumes that the narrow band consists of p orbitals of the O4 atoms (two equivalent atoms per unit cell). The added O1 atoms enter as O^{-1} ($v = 1$), and the O4 atoms fluctuate between O^{-2} and O^{-1} valence states, becoming O^{-2} for $\delta = 1$.

In summary, we reported on TEP measurements in $YBa_2Cu_3O_{7-\delta}$ between room temperature and 1200 K, in air and in oxygen at 1 bar. The TEP results were interpreted in terms of a narrow band model, where the carrier concentration depends on δ. The postulated narrow band is half filled for $\delta = 0$, and full for $\delta = 1$. Below 700 K, we cannot distinguish between the prediction of this model, and of a wide band model. Possible origins for such a narrow band were discussed.

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Note added in proof

In another publication [9], a narrow band, such as discussed here, is derived from a model which includes correlation effects on the band structure. This band has two states per unit cell, and originates mainly from the O2–O3 p-orbitals.